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Chemically prepared amorphous Fe-B particles: Influence of *p*H on the composition

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Fe-B alloys have been prepared by reduction of Fe ions by $NaBH_4$ in aqueous solutions. The boron content was found to vary with *p*H. For *p*H between 5 and 7, amorphous $Fe_{72}B_{28}$ powders were produced. Outside this *p*H range also α-Fe appeared in the samples. However, for *p*H = 8 amorphous $Fe_{86}B_{14}$ was formed, constituting about 90% of the sample.

I. INTRODUCTION

Amorphous Fe-B alloys are mostly prepared by using the liquid-quench technique,[1,2] where the product is in the form of ribbons. Because powders have an advantage over ribbons in that they are suitable for compaction processes, experiments to produce small particles have been carried out.[1] Only few methods are presently available for the preparation of ultrafine powders of amorphous Fe-B alloys. One method is an etching–sputtering method[3] and another is a chemical reduction method.[4]

Amorphous Fe-B particles prepared by reduction of Fe^{2+} ions by $NaBH_4$ in aqueous solutions have recently been studied extensively.[5-7] The magnetic hyperfine parameters, as deduced by ^{57}Fe Mössbauer spectroscopy, as well as the crystallization and Curie temperatures are very similar to those of ribbons with the same composition. Structural investigations by x-ray and electron diffraction, EXAFS, and Mössbauer studies have revealed that the particles indeed have an amorphous structure.[6]

Our first samples produced by the method of chemical reduction of transition metal ions with an alkaline-metal borohydride had boron contents of about 40 at. %,[4-6,8] with few exceptions.[9] A recent study of the effect of changing the concentration of the metal ion and the $NaBH_4$ solutions has shown that the boron content in the prepared particles may be lowered considerably.[7]

In this paper we present results of a systematic study of the effect of changing the *p*H of the Fe^{2+} ion solution while keeping the molar concentration of both the metal ion and $NaBH_4$ aqueous solutions constant. It turns out that the boron content depends sensitively on the *p*H of the metal ion solution.

II. EXPERIMENT

The Fe-B alloys were prepared by adding 200 ml of 0.1*M* $NaBH_4$ to 500 ml of 0.04*M* $FeSO_4$, with vigorous stirring, over a period of approximately 1 h. Samples were prepared with *p*H of the Fe^{2+} solution kept at values between 4 and 9, controlled by adding 0.1*M* HCl or NaOH during the sample production. The fluctuations of *p*H were less than 0.5. The samples were washed carefully with distilled water and acetone with the samples continuously covered with liquid in order to avoid oxidation in air.[6] Part of the sample was then transferred to a sample holder and immediately frozen to liquid nitrogen temperature. The remaining sample was dried and passivated in a flow of nitrogen gas containing 1000 ppm O_2. The passivated sample was analyzed for Fe and B contents by using photoabsorption spectroscopy and wet chemical analysis.

Mössbauer spectroscopy was performed with the sample at 80 K. For this purpose a constant acceleration spectrometer with a 50 mCi source of ^{57}Co in rhodium was employed. The velocity scale was calibrated from a room temperature measurement on a 12.5 μm α-Fe foil. The absorption lines in the Mössbauer spectra were fitted to Lorentzian lines by a least-squares method.

III. RESULTS

Figure 1 shows the Mössbauer spectra, obtained at 80 K, for the samples with *p*H between 4 and 9. The spectra for the samples prepared with *p*H equal to 5, 6, and 7 are similar to each other and consist of six broad absorption lines. A sample prepared with a *p*H of 8 is seen to result in a considerably larger hyperfine field. This spectrum consists of a sextet with broad absorption lines as the dominant component. An iron hydroxide is the main product when the *p*H is kept at about 9.

The magnetic hyperfine fields, deduced from least-squares fitting with sextets, are shown in Fig. 2. The spectra for the samples with *p*H kept at 5, 6, and 7 under the preparation were fitted with a single sextet with broad absorption lines, yielding a magnetic hyperfine field of about 25.5 T.

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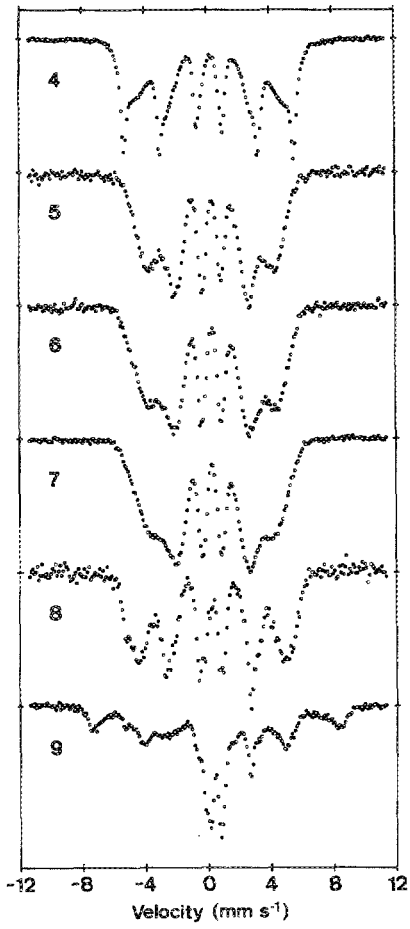

FIG. 1. Mössbauer spectra, obtained at 80 K, for Fe-B samples prepared with the pH kept at the indicated values.

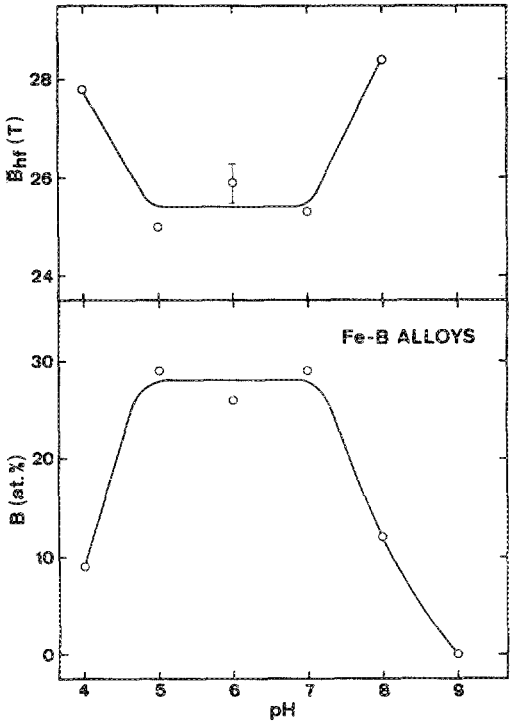

FIG. 2. The magnetic hyperfine field for the amorphous phases in the spectra and the overall boron content of the particles as a function of pH.

Fitting with a single sextet yielded a fair description of the spectra. The sample with $p\mathrm{H} = 4$ was fitted with two sextets; one with sharp lines, a hyperfine field of 33.7 ± 0.5 T, an isomer shift of 0.1 ± 0.1 mm s^{-1}, a negligible quadrupole shift, and a relative intensity of about 70% of the Mössbauer spectrum—and another sextet with broad lines and $B_{\mathrm{hf}} \simeq 27.8$ T. The $p\mathrm{H} = 8$ spectrum was fitted with two sextets and a doublet. The dominant sextet, with a relative area of about 90% of the Mössbauer spectrum, had broad absorption lines (FWHM = 1.5 mm s^{-1} for the outer lines) and $B_{\mathrm{hf}} \simeq 28.4$ T. The other sextet had $B_{\mathrm{hf}} = 33.4$ T and constituted a relative area of about 7%, while the doublet had an isomer shift of 1.2 mm s^{-1} and a quadrupole splitting of about 2.9 mm s^{-1}.

Figure 2 also shows the results of the chemical analysis. For pH equal to 5, 6, and 7 the samples contained about 28 at. % B. Outside this pH region the boron content decreased and for pH equal to 4 and 8 the overall boron content was found to be 9 and 12 at. %, respectively. No boron could be detected in the sample prepared with $p\mathrm{H} = 9$.

IV. DISCUSSION

Without control of pH during the reaction, the pH increases from an initial value of about 3 to a value of about 7. The pH fluctuates significantly during the reaction and its value depends on, e.g., the rate of mixing of the solutions. The boron content is about 28 at. % (Ref. 7) when using solutions identical to those in this work. For the pH kept at values between 5 and 7 during the reaction a similar composition is obtained (cf. Fig. 2). However, when forcing the pH outside this range by adding HCl or NaOH during the reaction, the boron content in the sample drops and reaches a value close to 10 at. % for pH equal to 4 or 8. Sharp absorption lines then appear in the Mössbauer spectra. These lines can be assigned to α-Fe in the samples.

The broad absorption lines in the spectra for pH between 5 and 7 reflect a distribution of hyperfine parameters, which is indicative of an amorphous structure. The absence of sharp lines in these spectra show that these samples are completely amorphous. The magnetic hyperfine field at 80 K is in agreement with that obtained on amorphous ribbons[10] prepared by the liquid-quench technique.

The Mössbauer spectrum at 80 K of the sample prepared with pH kept at 8 primarily consists of a sextet with broad lines, which is attributed to an amorphous phase. If the boron in the sample is present solely in this amorphous phase, it would contain about 14 at. % boron. The magnetic hyperfine field for the amorphous phase was deduced to be 28.4 ± 0.4 T, which is in good agreement with the 28.9 ± 0.3 T found for amorphous $Fe_{85}B_{15}$ ribbons at 80 K.[10] The linewidths are also similar.

Investigations are now undertaken where the pH is controlled between 7 and 8 in order to vary the boron content from about 30 at. % down to about 10 at. %. These results will be reported elsewhere.[11]

V. CONCLUSIONS

It has been demonstrated that the boron content in powders produced by chemical reduction of iron ions by $NaBH_4$ depends on the *p*H of the aqueous iron solution. A clear correlation between the boron content and the magnetic hyperfine field is found. An amorphous Fe-B alloy with a boron content as low as 14 at. % has been prepared by the reduction method.

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